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In re Application of: Michel PUECH

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For: A METHOD AND APPARATUS FOR ANISOTROPICALLY ETCHING
SILICON WITH A HIGH ASPECT RATIO

DECLARATION

I, Andrew Scott Marland, of 11, rue de Florence, 75008 Paris, France, declare that I am well acquainted with the English and French languages and that the attached translation of the specification and claims as originally filed on January 3, 2002 in respect of French patent application number 02/00032 is a true and faithful translation of that document.

All statements made herein are to my own knowledge true, and all statements made on information and belief are believed to be true; and further, these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any document or any registration resulting therefrom.



Date: November 21, 2006

Andrew Scott Marland



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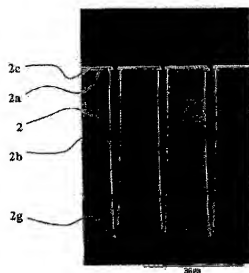


FIG. 1

Speed ($\mu\text{m}/\text{min}$)

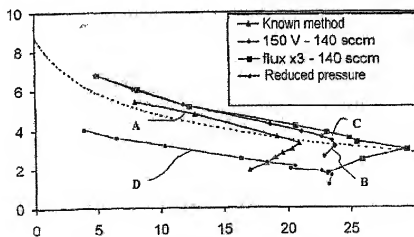


FIG. 2

Aspect ratio

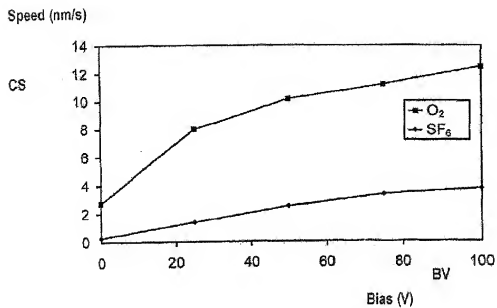


FIG. 3

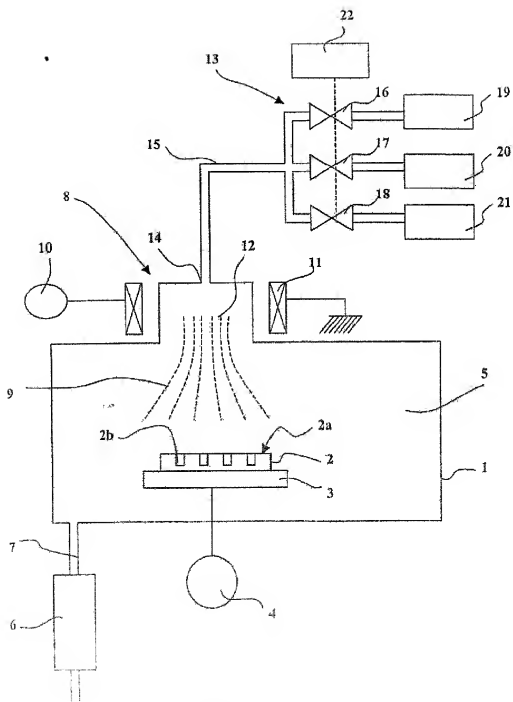


FIG. 4

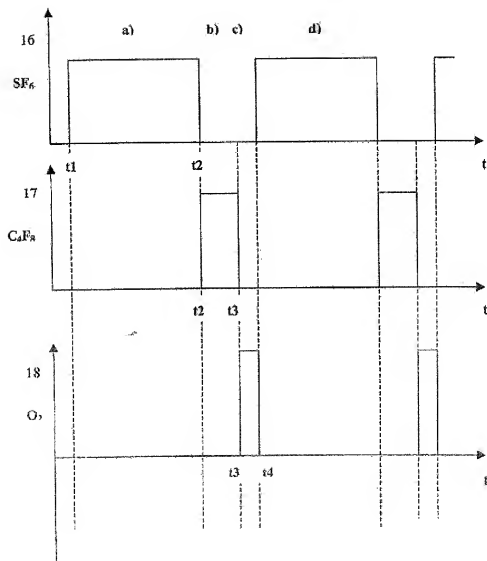
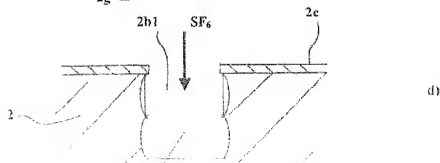
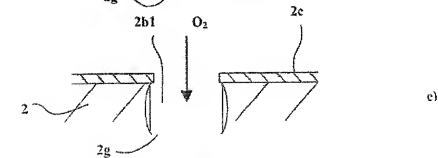
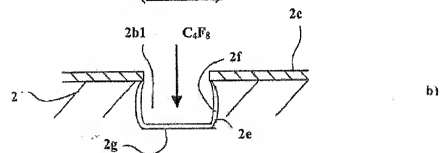
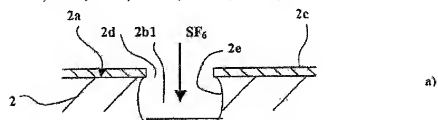
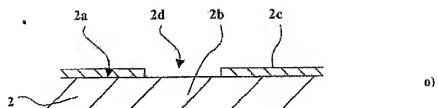


FIG. 5



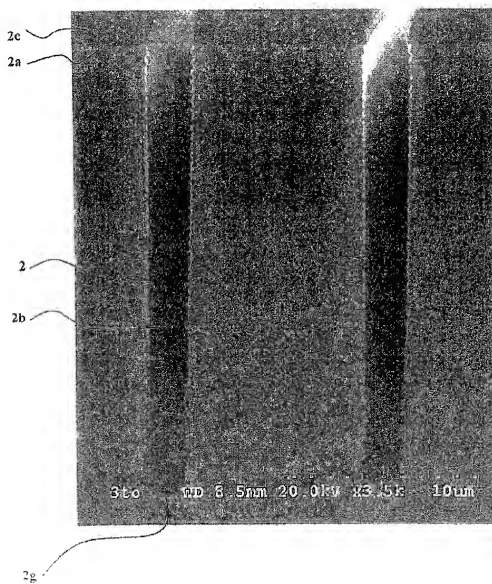


FIG. 7

A METHOD AND APPARATUS FOR ANISOTROPICALLY ETCHING
SILICON WITH A HIGH ASPECT RATIO

The present invention relates to methods and apparatuses used for making micro-relief at the surface
5 of substrates, in particular silicon substrates.

The invention relates more particularly to methods and apparatuses enabling such relief to be made by anisotropic chemical attack by plasma, for making silicon-based components, e.g. semiconductor components
10 for electronics, or parts for micromechanical components.

In the fabrication of such components, it is generally desired to make relief that reproduces on the surface of the substrate a plane, two-dimensional model with edges that are sharp and perpendicular to the plane.
15 For example, it might be desired to make a blind or through hole in a direction perpendicular to the general plane of the silicon substrate or "wafer", with the wall of the hole being parallel to its axis, and with the section of the hole being constant over its entire
20 height.

In the industrial field of micro-electro-mechanical systems (MEMS), there is ever increasing demand for structures of very high aspect ratio to be made in silicon substrates. By way of example, mention can be
25 made of the advantage that would be had if holes could be made having a diameter of 2 micrometers (μm) to 3 μm , and a depth of 100 μm to 200 μm , corresponding to an aspect ratio lying in the range 30 to 100, for the purpose of fabricating miniature high-capacitance capacitors for use
30 in mobile telephones.

Another example is the desire to make holes having a diameter of about 10 μm through the entire thickness of a silicon wafer in order to make connection sockets: once metal-plated, such holes would enable electrical
35 connections to be made with the outside without using gold wires, as is conventional. That would make it possible to provide connections that are highly

reproducible, and above all much shorter, thereby reducing stray inductance and thus presenting a great advantage for high frequency applications.

It is also possible to envisage making a hybrid of
5 MEMS with conventional integrated circuits in order to obtain MEMS including integrated signal processing.

The micromachining of silicon substrates is presently performed by plasma etching techniques. The technique that is the most widespread for this purpose at
10 present is fluorinated gas plasma etching as described in documents US 5 501 893 and US 4 985 114. That technique consists in protecting part of the silicon substrate by a mask, and in subjecting the substrate as protected in part in this way to an alternating succession of attack
15 steps using a plasma of etching gas, and of passivation steps using a plasma of passivation gas. During each attack step, the plasma of etching gas such as sulfur hexafluoride SF_6 makes cavities in those zones of the substrate that are not protected by the mask. During
20 each passivation step, the plasma of passivation gas such as a fluorocarbon gas, e.g. C_4F_8 , deposits a protective polymer film on the wall of the cavity. Each of these attack and passivation steps is of very short duration, e.g. a few seconds, and the passivation serves, during
25 the subsequent attack step, to ensure that the plasma of etching gas does not attack the side wall of the cavity. As a result, attack takes place selectively in the bottom of the cavity, after the plasma of etching gas has removed the protective polymer film from the bottom of
30 the cavity. Thus, in spite of the isotropic nature of the way in which silicon is attacked by a plasma of etching gas such as a fluorinated gas, the resulting etching of the silicon is quasi-anisotropic, fast, and selective.

35 However, when that technique is used to etch patterns having a high aspect ratio, such as trenches having a width of 2 μm to 3 μm , it is found that although

the etching profile is initially vertical, beyond a certain depth, the profile becomes slightly positive so that the two sides of the trench end up meeting each other, after which it is no longer possible to increase the depth of the trench. The result is shown in Figure 1 which is a photograph of a section of silicon substrate etched using that prior art method: in a substrate 2 having a surface 2a covered by a mask 2c, attempts have been made to provide a deep cavity 2b; it is not possible to reach a depth in excess of about 50 μm , the walls of the cavity 2b meeting at a bottom 2g of zero section that prevents any further etching. At present, and in practice, it is not known how to etch patterns with aspect ratios greater than about 20, i.e. having depth greater than 20 times their width or diameter.

There therefore exists a need to increase the aspect ratio of relief made by etching a silicon substrate.

To do this, a first solution has been to increase the energy of the ions during the etching step, by increasing the bias voltage of the substrate. This reduces the number of ions lost against the walls of the trench, and it is possible to benefit from a larger number of ions for breaking up the layer of polymer in the bottom of the trench. It has thus been possible to increase the aspect ratio a little, but only from a ratio of 20 to a ratio of 23. However, that solution presents the major drawback of increasing the rate at which the mask itself is attacked, which mask is made of silica or of photosensitive resin, thereby reducing the selectivity of the etching.

A second solution which has been devised is to increase the flux of ions reaching the surface of the substrate, in the hope that there will then be sufficient ions to break up the polymer film in the bottoms of the cavities. To do this, a first technique has been to increase the power of the plasma source. That enables the aspect ratio to be increased up to about 27, while

also degrading selectivity compared with the mask, as in the preceding solution. As an alternative, the substrate has been placed closer to the plasma source, and that also makes it possible to increase the aspect ratio up to about 27. However uniformity of etching is then degraded, i.e. the depth of etching varies as a function of the zone under consideration in the substrate.

A third solution that has been devised is to reduce the working pressure so as to increase the mean free path length of the particles, thereby reducing collisions between particles and increasing the directivity of ions. As in the first solution, that has made it possible to benefit from a larger number of ions for breaking up the polymer layer in the corners at the bottoms of the trench, and it has been possible to increase aspect ratio a little, up to a value of about 23. That solution does not enable aspect ratio to be increased significantly, and it presents the drawback of considerably reducing the rate at which the silicon is etched, which is contrary to the looked-for object.

The results of those tests are summarized in Figure 2. Curve A represents the usual method of etching by alternating steps of attack by means of a plasma of fluorinated gas and steps of passivation by a plasma of fluorocarbon gas, in accordance with document US 5 501 893. Curve B shows the result obtained by increasing the bias voltage of the substrate, i.e. by increasing the bombardment energy of the plasma ions. Curve C shows the result obtained by moving the substrate closer to the plasma source. Curve D shows the result obtained by reducing the pressure of the atmosphere in the etching chamber by a factor of 2.

In each case, each curve reveals how etching speed or the speed at which cavities are excavated, varies progressively as a function of the depth the cavity has reached. It can be seen that for each curve, the etching speed decreases progressively as a function of cavity

depth. For each curve, a depth maximum is reached, and this maximum determines the maximum aspect ratio that can be achieved by the method. Curve A shows a maximum aspect ratio of about 21. Curve B shows a maximum aspect ratio of about 23. Curve C shows a maximum aspect ratio of about 29. Curve D shows a maximum aspect ratio of about 23.

An object of the present invention is to implement etching of silicon with anisotropy that is almost perfect, without undercut attack and without the cavity tapering progressively, down to depths that are considerably increased, making it possible to achieve aspect ratios greater than 30.

Preferably, the invention also seeks to implement such etching at speeds that are at least as fast if not faster than the etching speeds achieved by known methods of alternating steps of attack by fluorinated gas plasma and passivation by fluorocarbon gas plasma.

To achieve these objects and others, the invention provides a method of etching silicon anisotropically, in which a silicon substrate protected in part by a mask is subjected to an alternating succession of attack steps using a plasma of etching gas to make cavities in zones of the substrate that are not protected by the mask, and passivation steps using a plasma of passivation gas for depositing protective polymer on the walls of the cavities that result from the attack steps,

the method of the invention further comprises selective depassivation pulse steps in which the protective polymer deposit is subjected to the action of a plasma of cleaning gas that removes the protective polymer from the bottom zones of the cavities and that is more effective than the etching gas.

By cleaning off the protective film in the bottom zones of the cavities more effectively, the drawback of the walls of the cavity coming progressively closer together in the bottom of the cavity is avoided, thereby

enabling aspect ratios that are considerably greater to be achieved.

In an implementation, the method includes a selective depassivation pulse step after each passivation step.

Advantageously, each selective depassivation pulse step does not overlap the preceding passivation step, and does not overlap the following attack step.

Advantageously, the etching gas may be a fluorine gas such as SF_6 , CF_4 , or NF_3 . The best results appear to be obtained with SF_6 .

Advantageously, the passivation gas may be a fluorocarbon gas such as CHF_3 , C_2F_6 , C_2F_4 , C_2F_8 , or mixtures thereof.

Under all circumstances, the cleaning gas may advantageously contain oxygen. As a cleaning gas, it is possible to use at least one of the following gases: O_2 , SO_2 , CO , CO_2 , NO , NO_2 , N_2O , and mixtures thereof.

In another aspect, the invention provides apparatus for anisotropic etching of a silicon substrate, to implement a method as defined above, the apparatus comprising:

- a gastight enclosure shaped to receive and contain a substrate for etching;
 - means for creating and maintaining a suitable vacuum in the enclosure;
 - gas injection means for selectively injecting into the enclosure etching gas, passivation gas, and cleaning gas for programmed durations and at programmed flow rates;
 - means for generating a plasma in the enclosure facing the surface of the substrate that is to be etched;
 - means for biasing the substrate; and
 - control means for controlling the gas injection
- means to perform the successive etching, passivation, and depassivation steps.

In another aspect, the invention enables silicon-based components to be made having micro-relief presenting an aspect ratio of more than 30, e.g. by using a method as defined above. Such components are themselves novel in character since it has not been possible to make them until now.

Other objects, characteristics, and advantages of the present invention appear from the following description of particular implementations, given with reference to the accompanying figures, in which:

10 · Figure 1, described above, shows the profile of trenches made using a prior art etching method;

 · Figure 2 is a graph plotting curves of etching speed as a function of aspect ratio for various prior art etching methods;

15 · Figure 3 is a graph plotting the speed with which a protective polymer film is attacked, as a function of the substrate bias voltage, firstly for attack using SF_6 , and secondly for attack using an oxygen plasma;

20 · Figure 4 is a diagram of etching apparatus constituting an embodiment of the invention;

 · Figure 5 is a timing chart showing the steps of the method in an implementation of the invention;

25 · Figure 6 is a diagram showing the way in which a cavity is formed during a sequence of four successive steps in the method of Figure 5; and

 · Figure 7 shows the profiles of trenches being made by an etching method of the invention.

Consideration is given initially to the etching apparatus of the invention, e.g. in the embodiment shown in Figure 4.

Such apparatus comprises a gastight enclosure 1 shaped to receive and contain a substrate 2 for etching. The substrate 2 is placed on a support 3, itself negatively biased relative to ground by bias means comprising a bias source 4.

A vacuum generator device 6 is connected to the enclosure 1 via a pipe 7, and comprises, for example, a primary pump and a secondary pump, enabling a suitable vacuum to be created and maintained inside the enclosure 1.

The substrate 2 is oriented in the enclosure 1 in such a manner that its surface 2a for working is visible. By way of example, it is desired to make cavities such as the cavity 2b in the surface 2a.

Facing the surface 2a that is to be machined, there are plasma generation means 8 for generating a plasma 9 that is directed towards the surface 2a that is to be machined and that is attracted by the substrate 2 biased by the bias source 4. In outline, the plasma generation means 8 comprise a microwave or radiofrequency generator 10 that acts, via a transducer or radiofrequency applicator 11 to excite atoms of gas in a plasma generation zone 12.

The apparatus also includes means 13 for selectively injecting into the enclosure 1 etching gas, passivation gas, and depassivation gas. Thus, these gas injection means 13 comprise a gas inlet 14 for admitting gas into the enclosure 1, preferably upstream from the plasma generation zone 12, the gas inlet 14 being connected by pipes 15 and control valves 16, 17, and 18 respectively to an etching gas source 19, to a passivation gas source 20, and to a cleaning gas source 21. The control valves 16, 17, and 18 are actuated by control means 22 to control the injection of gas in the successive steps of etching, passivation, and depassivation in the method that is described below.

Reference is now made to the diagrams of Figure 5, which show respectively the times during which the valve 16 is open to admit etching gas, the times during which the valve 17 is open to admit passivation gas, and the times during which the valve 18 is open to admit cleaning gas. It can be seen that the steps of the method are

pulse steps, i.e. of limited duration between stop periods.

It can be seen that the first step a) of attack consists in opening the valve 16 to generate a plasma 9 of etching gas. The first step a) of attack is followed by a non-overlapping, second step b) of passivation during which the valve 16 is closed and the valve 17 is open in order to generate a plasma 9 of passivation gas. Thereafter, the valve 17 is closed, and during a selective depassivation step c), the valve 18 is opened to generate a plasma 9 of cleaning gas. Thereafter the valve 18 is closed and the operations are restarted in a step d) by opening the valve 16 again to generate a plasma of etching gas, and so on.

In the embodiment shown in Figure 5, the successive steps a), b), c), and d) do not overlap one another. Nevertheless, without going beyond the ambit of the invention, it would be possible to make provision for a step c) that overlaps one and/or the other of adjacent steps b) and d).

During step a) of generating a plasma of etching gas, there is admitted into the enclosure 1 an etching gas of the fluorinated gas type, such as SF_6 , CF_4 , or NF_3 , for example. Excellent results are obtained using sulfur hexafluoride SF_6 . During this step, the atoms of fluorine generated by the plasma attack the exposed surface area of silicon in isotropic manner. Figure 6 is a diagram showing the action of the plasmas on the substrate: the substrate 2 is shown in fragmentary section at a large scale, at the location where a cavity 2b is to be made: the substrate 2 is covered by a mask 2c which includes an opening 2d in register with the cavity 2b that is to be made. Thus, under the opening 2d, the surface of the substrate 2 remains visible and accessible to the plasma.

In view o) of Figure 6, the substrate 2 is shown before etching.

In view a) of Figure 6, there is shown the action of the plasma of etching gas SF_6 attacking the silicon of the substrate 2 isotropically in register with the opening 2d so as to make a first segment 2b1 of the cavity 2b. The duration of the etching step between instants t_1 and t_2 in Figure 5 is selected so that the first segment 2b1 of the cavity presents a shape that differs little from the desired shape, i.e. with a side wall 2e that is substantially perpendicular to the surface 2a of the substrate. A first segment 2b1 having a depth of a few micrometers can be appropriate. It is possible to select etching parameters of the kind commonly used, for example the substrate 2 may be biased at about 20 volts (V) to 80 V, the pressure of the gaseous atmosphere 5 inside the enclosure 1 may be about 10 pascals (Pa) to 100 Pa, and the flow rate of the etching gas may be about 10 standard cubic centimeters per minute (sccm) to 200 sccm.

During passivation step b), a plasma of passivation gas is generated by using a fluorocarbon gas such as CHF_3 , C_2F_6 , C_3F_8 , or C_4F_8 . The pressure of the atmosphere 5 in the enclosure 1 is similar to that in step a) and the passivation gas flow rate lies in the range 50 sccm to 300 sccm. During this step, as shown in view b) of Figure 6, the plasma of passivation gas causes a protective polymer film 2f to be formed over the entire inside surface of the first segment 2b1 of the cavity, i.e. both over its side wall 2e and its bottom 2g. The duration between the start instant t_2 and the end instant t_3 of step b) is selected so as to cause the thickness of the protective film to be satisfactory, for example of the order of a few nanometers (nm) to a few tens of nm.

During step c), a plasma of cleaning or depassivation gas is generated, which gas is selected so as to provide cleaning of the polymer that is more effective than that which is provided by the etching gas, and serves to remove polymer from the bottom zone 2g of the cavities 2b in selective manner. Good results have

been obtained by using a cleaning gas containing oxygen, e.g. a cleaning gas containing at least one of the following gases: O_2 , SO_2 , CO , CO_2 , NO , NO_2 , N_2O .

5 The substrate 2 is preferably simultaneously biased by the bias source 4 so as to attack the ions of oxygen to the substrate 2.

It has been possible to measure the speed at which the polymer film is etched by the oxygen plasma and to compare this speed with that obtained by the plasma of fluorinated gas SF_6 that corresponds to the etching step. This comparison is shown in Figure 3. It can be seen that the curve corresponding to the oxygen plasma enables a cleaning speed CS to be obtained that is at least four times faster than the speed obtained when cleaning using sulfur hexafluoride SF_6 , at all bias voltages BV between 0 and 100 V. Consequently, the oxygen plasma is at least four times as effective as the plasma of fluorinated gas such SF_6 for cleaning the polymer film. In addition, a plasma of gas containing oxygen atoms benefits not only from the oxidizing effect of the ions, but also from the oxidizing effect of atoms which are neutral particles with an isotropic trajectory. It is found that the cleaning step makes it possible also to remove polymer film from the vertical sides of the cavity in the vicinity of the bottom of the cavity, thus ensuring that the patterns do not taper and making it possible to reach higher aspect ratios.

Since the time taken to remove the polymer film is greatly reduced, the time available for the etching step is correspondingly increased, and this makes it possible to increase the overall speed of etching, and thus to increase the productivity of the equipment.

During the pulse step of selective depassivation or cleaning, the substrate 2 is biased with a voltage close to that used during the attack step, typically in the range 20 V to 120 V, and advantageously in the range 20 V to 80 V, so as to attract the plasma ions. The pressure

of the atmosphere 5 surrounding the substrate 2 lies in the range 0.5 Pa to 10 Pa, and preferably lies in the range 2 Pa to 5 Pa. The flow rate of the cleaning gas lies in the range 10 sccm to 100 sccm, and the duration
5 of step c) is selected to be just sufficient to ensure effective cleaning of the bottom zones 2g of the cavities 2b.

As can be seen in view c) of Figure 6, the depassivation step by the action of the plasma of oxygen
10 O₂ serves to remove effectively and quickly the polymer film from the bottom 2g of the first segment 2b1 of a cavity.

Thereafter, during step d), an attack step is performed again similar to step a), by the action of the
15 plasma of the etching gas SF₆, thereby making a second segment 2b2 of the cavity 2b. Thereafter, there follows a pulse step of passivation, and a step of depassivation, and so on.

In practice, the duration of the pulse steps c) for selective depassivation can be determined as a function of the duration of the preceding passivation step b). The thicker the polymer film, the longer the time required for the selective depassivation pulse step.

Furthermore, the duration of the selective
25 depassivation pulse step may be selected to increase from one depassivation step to another during the process of etching a single substrate 2. As shown in Figure 1, the initial etching steps enable a cavity to be made having a side wall that is substantially vertical up to an aspect
30 ratio of about 20 without there being any need to use lengthy cleaning steps in order to conserve a constant section for the cavity. The advantage of the depassivation step is then merely that of increasing the speed of the method. However, thereafter, it becomes
35 essential to use the depassivation step in order to guarantee that an aspect ratio in excess of 20 or 30 can be achieved. It is therefore possible to consider using

depassivation steps of duration that is progressively longer with increasing aspect ratio, or indeed depassivation steps in increasing numbers, for example rising from one passivation step for three attack and
5 passivation steps, to one depassivation step for two attack and passivation steps, and passing finally to one depassivation step for one attack and passivation step.

Also, in the invention, it is possible to provide for the bias voltage applied to the substrate 2 to
10 increases progressively from one depassivation step to another during the process of etching a substrate 2.

The method of the invention makes it possible simultaneously to obtain aspect ratios that are considerably greater than those obtained with prior art
15 methods, while guaranteeing good selectivity with respect to photoresist masks, while also increasing the overall speed of etching.

The effect obtained is shown in Figure 7, which is a photograph of a section of a silicon substrate after an
20 operation of partial etching using a method of the present invention. There can be seen the substrate 2 whose surface 2a is covered by a mask 2c. The cavities 2b that are being etched present side walls that are substantially vertical, such that their bottoms 2g remain
25 of sufficient cross-section to make additional etching possible for increasing the depth of the cavities 2b, thereby increasing their aspect ratio.

The present invention is not limited to the embodiments described explicitly above, but it includes
30 the variations and generalizations that are within the competence of the person skilled in the art.

CLAIMS

1. A method of etching silicon anisotropically, in which a silicon substrate (2) protected in part by a mask (2c) is subjected to an alternating succession of attack steps (a) using a plasma of etching gas to make cavities (2b) in zones of the substrate that are not protected by the mask (2c), and passivation steps (b) using a plasma of passivation gas for depositing protective polymer (2f) on the walls of the cavities (2b) that result from the attack steps,
- the method being characterized in that it further comprises selective depassivation pulse steps (c) in which the protective polymer deposit (2f) is subjected to the action of a plasma of cleaning gas that removes the protective polymer (2f) from the bottom zones (2g) of the cavities (2b) and that is more effective than the etching gas.
2. A method according to claim 1, characterized in that it includes a selective depassivation pulse step (c) after each passivation step (b).
3. A method according to claim 2, characterized in that each selective depassivation pulse step (c) does not overlap the preceding passivation step (b), and does not overlap the following attack step (d).
4. A method according to any one of claims 1 to 3, characterized in that the etching gas is a fluorine gas such as SF_6 , CF_4 , or NF_3 .
5. A method according to any one of claims 1 to 4, characterized in that the passivation gas is a fluorocarbon gas such as CHF_3 , C_2F_6 , C_2F_4 , or C_4F_8 .
6. A method according to any one of claims 1 to 5, characterized in that the cleaning gas contains oxygen.

7. A method according to claim 6, characterized in that the cleaning gas comprises at least one of the following gases: O_2 , SO_2 , CO , CO_2 , NO , NO_2 , N_2O .

5

8. A method according to any one of claims 1 to 7, characterized in that during the selective depassivation pulse step (c), the substrate (2) is biased so as to attack the ions of the plasma.

10

9. A method according to claim 8, characterized in that the substrate (2) is biased by a voltage close to the voltage used during the attack step (a), typically in the range 20 V to 100 V, advantageously in the range 20 V to 80 V.

15

10. A method according to claim 8 or claim 9, characterized in that the bias voltage applied to the substrate (2) is increased progressively from one depassivation step to another during the process of etching a substrate (2).

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11. A method according to any one of claims 8 to 10, characterized in that during the selective depassivation pulse step (c), the pressure of the atmosphere (5) surrounding the substrate (2) lies in the range 0.5 Pa to 10 Pa, and preferably in the range 2 Pa to 5 Pa.

25

12. A method according to any one of claims 1 to 11, characterized in that the duration of the selected depassivation steps (c) is selected to be just sufficient to ensure effective cleaning of the bottom zones (2g) of the cavities (2b).

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13. A method according to any one of claims 1 to 12, characterized in that the duration of the selected

35

depassivation pulse step (c) is determined as a function of the duration of the preceding passivation steps (b).

14. A method according to any one of claims 1 to 13,
5 characterized in that the duration of the selected depassivation pulse step (c) increases from one depassivation step to another during the process of etching a substrate (2).
- 10 15. Apparatus for anisotropically etching silicon substrates (2), by implementing a method according to any one of claims 1 to 4, the apparatus comprising:
- a gastight enclosure (1) shaped to receive and contain a substrate (2) for etching;
 - 15 · means (6, 7) for creating and maintaining a suitable vacuum in the enclosure (1);
 - gas injection means (13) for selectively injecting into the enclosure (1) etching gas, passivation gas, and cleaning gas for programmed durations and at programmed
20 flow rates;
 - means (8) for generating a plasma (9) in the enclosure (1) facing the surface (2a) of the substrate (2) that is to be etched;
 - means (4) for biasing the substrate (2); and
 - 25 · control means (22) for controlling the gas injection means (13) to perform the successive etching, passivation, and depassivation steps.
16. A silicon-based component having micro-relief (2b)
30 presenting an aspect ratio greater than 30, made using a method according to any one of claims 1 to 14.